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R.A. Dobbins, Principal Investigator

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)

Division of Engineering
Brown University
PRovidence, RI 02912

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12a. DISTRIBUTION / AVAILABILITY STATEMENT

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13. ABSTRACT *(Maximum 200 words)*

This research has provided an understanding of the formation of earliest soot particles (soot precursor particles) in combustion processes, and thus indicates strategies to intervene in their formation in various types of combustion devices. Major progress was achieved in characterizing the chemical composition and the carbonization of soot precursor particles that have been found in laboratory flames. The use of TEM has permitted the observation of precursor particles in flames fueled by CH_4, C_2H_4 and C_2H_2. The transformation of the liquid-like precursor particles into solid clustered aggregates by the carbonization process was displayed. The conversion kinetics of carbonization were studied because this process converts the young more easily oxidized young particles into the more inert carbonaceous aggregates that are likely to be released to the surroundings. A major effort was in the area of chemical analysis of the precursor particles as studied by use of the LAMMA-500 instrument at the NIST. These studies revealed the precursor particles to consist of PAHs and that these compounds are members of the stabilomer classes predicted by Stein and Fahr to be the most chemically stable. Our last task has related to the development of crystallinity in precursor particles and in carbonaceous aggregates formed in hydrocarbon combusion.

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SOOT EVOLUTION AND CONTROL

FINAL PROGRESS REPORT

RICHARD A. DOBBINS
PRINCIPAL INVESTIGATOR

4 DECEMBER 1998

U. S. ARMY RESEARCH OFFICE

GRANT NO. DAAHO4-95-1-0429

DIVISION OF ENGINEERING
BROWN UNIVERSITY

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(1.) STATEMENT OF PROBLEM STUDIED:

Carbonaceous soot and smoke released by military vehicles is an indication of incomplete combustion of fuel and, additionally, constitutes both an undesirable detection signature under combat conditions and a pollution source under both combat and noncombat conditions. The purpose of this research work has been to achieve a more detailed understanding of the chemical and physical processes that are involved in the formation of particulate material by hydrocarbon fuels. The role of the initial particulate stage, the precursor particles, has been studied and elucidated in detail. Strategies for the elimination of the particulate product of combustion are enumerated including the possibility of the oxidation of the nascent, more reactive precursor particles. Rate data on the process of carbonization by which precursor particles are converted to carbonaceous soot was derived from our experiments.

(2.) SCIENTIFIC PROGRESS AND ACCOMPLISHMENTS:

A. Soot Precursor Particles In Hydrocarbon Flames:

Early TEM observations revealed the presence of young isolated particles low on the axis of the diffusion burner fueled by methane, ethene or acetylene. These observations were consistent with the reports in the literature, which were often disputed by reputable researchers, of a liquid droplet stage as intermediate stage between gaseous species and soot aggregates. The TEM micrographs showed the transformation (from isolated precursor particles to clustered aggregates) to occur between Z=30 and 40 mm in the ethene flame. This discovery opened a entirely new avenue of investigations of soot formation processes that is being pursued by various research investigators.

B. LMMS Analysis of Particulate Material:

Our earliest analyses of particles captured on the centerline of the ethene flame by thermophoretic sampling were conducted in collaboration with R. A. Fletcher of the NIST using the LAMMA-500. The initial tests revealed that the precursor particle contained mainly PAHs whose dominant masses were 252, 276, and 300 amu and that these species disappeared when clustered aggregates were formed. This metamorphosis of precursor particles to clustered aggregates was found to be accompanied by a decrease of hydrogen mole fraction from 0.35 to 0.15.

C. Carbonization Rate of Soot Precursor Particles:

The particle transformation constitutes the carbonization process which has been described in the carbon literature with the finding that the process complies with first order Arrhenius reaction kinetics. Studies of the particle transformation in diffusion flames fueled by ethene diluted with nitrogen were conducted. Careful observation of the temperature profiles of these flames were conducted using a modified version of rapid insertion thermocouple thermometry. These studies lead to rate constants of E=113 kJ/mol and $A=1.78 \times 10^{+6}$ s^{-1}. This rate data permits the calculation of the time allowed for the oxidation of precursor particles prior to their transformation to carbonaceous aggregates at a given temperature.

D. Precursor Particle Evolution in Hydrocarbon Flames:

A systematic analysis of the precursor particle composition was conducted at the flames heights above burner of Z=20, 30, 35 and 40 mm by means of the LAMMA-500. These studies lead to the conclusion that the dominant species were PAHs predicted to be chemically most stable (stabilomers) under flame conditions by Stein and Fahr in 1985. The presence of the same stabilomer PAHs in studies of others embracing a wide range of combustion processes lead to the conclusion that the stabilomer PAHs represents the path through which all carbonaceous soot is formed in flames. This observation accounts for the chemical commonality of the carbonaceous soot from a wide range of fuels and combustion processes.

E. Precursor Particles in the Deuterated Ethene Flame:

Our analyses of precursor particles showed disparate species with identical masses that could not be unambiguously identified -- a not uncommon problem in the art/science of mass spectrometry of hydrocarbon compounds. This uniqueness issue is resolved by the substitution of deuterated ethene C_2D_4 for the normal fuel causing a mass shift of compound C_xH_y of exactly y mass units *only if* the proper values of x and y have been identified. Our project received a donation of five liters of the valuable C_2D_4 from the Cambridge Isotope Laboratories, Inc. of Andover, MA on the basis of a competitive grant program. The results of these tests showed that the substitution of deuterium for hydrogen displaced the masses of the resulting C_xD_y compounds by exactly y mass units which is the number of hydrogen atoms per molecule. This outcome provides very strong evidence that the chemical formulae of the PAHs have been accurately determined.

A computerized literature search reveals these tests to constitute the first use of a pure deuterated fuel in a combustion experiment. The C_xD_y compounds so created are polycyclic aromatic deuterocarbons and are the chemical analogues of PAHs with the corresponding values of x and y. This flame was similar in appearance to the C_2H_4 flame but did have a noticeably lower flame radiance. The LMMS analysis showed smaller soot samples to be recovered as is consistent with a lower soot production.

F. Dark Field TEM Analysis of Soot Precursor Particles and XRD Analysis of Carbonaceous Soot:

Dark field TEM images have been used recently to show the development of crystallinity in precursor particles. These are secured when the electron beam axis is tilted to hide the transmitted beam and allow scattered electrons to make a visible image. Crystals consisting of coplanar PAHs that are perpendicular to direction of tilt and that satisfy the Bragg condition will show bright reflections corresponding to the 002 reflections. We have secured a sequence of micrographs in the ethene diffusion flame from Z=25 mm to 40 mm that show particle images in both bright and dark field TEM. These micrographs display the development of crystallinity initially to occur within the precursor particles prior to their conversion to form the more carbonaceous clustered aggregates.

Large soot samples from the smoking ethene flame have been analyzed by X-ray diffraction, as well as by bright and dark field TEM, to derive the crystallographic interplanar distances of the crystal structure. It is found that the crystallogenesis process is

first evident in the precursor particles which display bright domains in dark field TEM. This work remains to be reported as discussed below.

(3.) LIST OF ARTICLES PUBLISHED DURING THE GRANT PERIOD:
"Laser Microprobe Analysis of Soot Precursor Particles and Carbonaceous Soot" by R. A. Dobbins, R. A. Fletcher and W. Lu in *Combustion and Flame* 100, 301-309, (1995). "The Carbonization Rate of Soot Precursor Particles" by R. A. Dobbins, G. J. Govatzidakis, W. Lu and A. F. Schwartzman in *Combustion Science and Technology*, Vol. 121, pp. 103-121 (1996). "The Early Particle Formation in Hydrocarbon Flames" by R. A. Dobbins in *Physical and Chemical Aspects of Combustion - A Tribute to Irvin Glassman,* Vol. 4, pp.107-133, Vol. 4 of the *Combustion Science and Technology Book Series*, Gordon and Breach Publishers (1997). "The Evolution of Soot Precursor Particles in a Diffusion Flame" by R. A. Dobbins, R. A. Fletcher, and H.-C. Chang, in *Combustion and Flame*, Vol. 115, 285-298, 1998. "Mass Spectrometry of Particles Formed in a Deuterated Ethene Diffusion Flame", R. A. Fletcher, R. A. Dobbins and H.-C. Chang in *Analytical Chemistry* 70, 2745-2749, 1998.

(4.) SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT DURING THE REPORTING PERIOD: Prof. Richard A. Dobbins, Principal Investigator; Dr. H.-C. Chang was associated with the grant from 1 November 1995 through 31 May 1996. Dr. Huxiong Chen a Postdoctoral Research Associate joined the research project on 1 June 1997 through 31 December 1997. Ms. J. L. Yu, a junior level engineering student, provided laboratory assistance from September to December 1996. Mr. A. F. Schwartzman, Senior Research Engineer, briefly conducted HRTEM on particle samples and supervised the training of personnel to operate the Philips 420 STEM Electron Microscope. Mr. William D. Lilly, Senior Technical Assistant, provided technical skills in modifying experimental equipment as required.

(5.) REPORT OF INVENTIONS: None.

(6.) TECHNOLOGY TRANSFER:

An informal cooperation has been established with research personnel of the Cummins Engine Co., the NIST, and Brown University. In this arrangement, diesel particle samples were obtained from Cummins by means of grid holders designed and fabricated at Brown University. The particle samples were obtained from a diesel engine operating at several different engine speeds and EGR rates. These samples were analyzed by R. A. Fletcher at the NIST on the LAMMA-500. The mass spectra of the diesel soots collected under various engine operating conditions have recently been forwarded to Brown for study by the undersigned in consultation with R. A. Fletcher. The results of this analysis and study will be shared by the participants in this cooperative study.

All of the research results reported herein were made possible by the development in our laboratory of the thermophoretic sampling method as reported by the undersigned and C. M. Megaridis now at the University of Illinois at Chicago. This sampling method is now in use at twenty industrial and university laboratories in the US and abroad for the study of particle formation in combustion processes.

(7.) ADDITIONAL RESEARCH REPORTING:

In addition to the publications described above, a number of oral presentations have ensued. Recent oral papers include: A platform paper entitled "The Evolution of Soot Particles in a Diffusion Flame" was presented by R. A. Dobbins at the annual technical meeting of the American Association for Aerosol Research in Denver on October 14, 1997. A poster paper was presented at the same meeting entitled "Laser Mass Analysis of Aerosol Formed in a Deuterated Ethene Diffusion Flame". The co-authors of these papers included R. A. Fletcher and H.-C. Chang. A paper entitled "Particle Sampling From a Deuterated Ethene (C_2D_4) Flame" by the same authors was presented at the Eastern States Section of the Combustion Institute on October 27, 1997 at Hartford. A recent paper entitled "Crystallogenesis of Particles formed in Hydrocarbon Combustion" has been submitted to the March 1999 Meeting of the US Sections of the Combustion Institute in Washington, DC.

(8.) RESEARCH REMAINING TO BE REPORTED:

Samples of diesel soot have been received from the Cummins Engine Co. and were forwarded to the NIST for analysis by the LAMMA-500. The report on these results is in preparation. Large soot samples were obtained from the smoking C_2H_4 flame to afford X-ray diffraction studies which will be reported at an appropriate venue

Prepared by

4 December 1998

Richard A. Dobbins
Principal Investigator
Professor of Engineering
(Research)